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THE METHANISATION OF COAL GAS
INFORMATION OBTAINED FROM
Dr. MARTIN OF RUHRCHEMIE A.G. AND
Dr. TRAENCKNER OF RHURGAS A.G.

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The Methanisation of Coal Gas
Information obtained from Dr. Martin of
Ruhrchemie A.G. and from Dr. Traenckner
of Ruhrgas A.G.

Reported by

E.T. Wilkins

on behalf of

British Ministry of Fuel and Power and the

U.S. Technical Industrial Intelligence Committee.

CIOS Target Nos. 30/5.01, 30/6.11
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Personnel of Team

H.H. Lowry (U.S.) T.I.I.C.
H.J. Rose (U.S.) T.I.I.C.
E.T. Wilkins (British) M.F.P.

The Methanisation of Coal Gas

Information obtained from Dr. Martin of
Ruhrchemie A.G. and from Dr. Traenckner
of Ruhrgas A.G.

Object of Investigation. learn of recent German developments in the catalytic synthesis of methane from gases containing carbon monoxide and hydrogen.

Locations and dates of interrogations. Dr. Traenckner, director of Ruhrgas A.G., was interviewed at Ruhraller G, Essen, on 4th July, 1945, by Drs. Lowry, Rose and Wilkins.

Dr. Martin, director of Ruhrchemie A.G., and Mr. Hanisch, chemist, were interviewed on 5th July by Dr. Wilkins at the Oberhausen-Holten works. Dr. Traenckner was also present on this occasion.

Summary. A process has been developed for effecting the catalytic methanisation of coal gas, and plants for operating this process on the scale of 6,200 cu.ft./hr. have been installed at road-side filling stations. These stations supplied the processed gas compressed to 300 atmospheres for use as motor fuel.

The objects of the process were (a) to enhance the calorific value of readily available town's gas to 650 B.Th.U./cu.ft. and (b) to remove constituents which caused deterioration of the high pressure cylinders.

Details of the catalyst, the design, method of operation and performance of the plant were elicited, and some items of the equipment inspected.

The locations of six methanisation plants are given in the report. None of these was visited.

General. The process was developed by Ruhrchemie, who remained responsible for the technical side of the project and for the supply of catalyst. The plants were installed by Ruhrgas at filling stations for the purpose of 'methanising' town's gas, and charging it into cylinders at about 300 atmospheres pressure, for use as motor fuel. The A.G. der Kohlenwertstoff Verbannde of Bochum, as distributors of liquid and other motor fuels, also had some interest in the commercial application of the process.

From the chemical standpoint the process had two objectives:

1. To make the town's gas into a better motor fuel by increasing its calorific value. This increase was said to be from between 450 and 500 to between 650 and 850 B.Th.U./cu.ft.

2. To remove constituents of the gas which had a corrosive effect on high-pressure storage vessels. These constituents were carbon monoxide, hydrocyanic acid, sulphur compounds and oxygen.

When the success of the process had been demonstrated in a pilot plant at Altenessen, arrangements were made for a large number of plants to be constructed. By the end of the war the following plants had been completed :

1. Altenessen (practically destroyed)
2. Dusseldorf gasworks) plants completed
3. Dresden) and used.
4. Opel works, Frankfurt-Russelheim) Plants completed
5. Carolinen Glück Colliery, Bochum) but not used.
6. Kokerei Zollverein, Gelsenkirchen - no details available.

Each of these plants was of essentially the same design which consisted of a basic unit capable of producing 180 cu.m. (6,200 cu.ft.) of gas per hour. If a greater output was required the plant was duplicated.

The plants were designed to be foolproof so that they could be operated by a non-technical filling-station attendant. They were also capable of being easily started and stopped as required by the erratic demand by road vehicles.

Details of the plant. The processing of the gas involved the following treatments :-

1. Boosting town's gas to a pressure sufficient to pass it through the plant.
2. Heating to a temperature of 400-450°C.
3. Addition of steam (in certain cases).
4. Catalytic conversion of organic sulphur compounds to hydrogen sulphide.
5. Cooling.
6. Removal of hydrogen sulphide.
7. Methanisation.
8. Cooling.
9. Compression to 350 atmospheres.

A flow diagram is given as Fig. 1.

Methane reactor: Details of the methanisation reaction vessel are given as Fig.2. In this unit the catalyst was contained in 158 steel tubes about 28 m.m. bore x 165 cm. long. These tubes were surrounded by a water jacket which served both to take away the heat of the reaction when the plant was in operation, and, when the plant was shut down, to maintain the catalyst at a temperature at which methane synthesis would be positively started when the process gas was turned on.

A reactor which was examined at Oberhausen-Holten had been made by Gottfried Bischoff, Essen. The name plate also said that it had been tested to 30 atmospheres.

The maximum working pressure in the water jacket was said to be 20 atmospheres (215°C), with a normal temperature of 160-180°C.

Gas heating was employed to keep the reactor hot when it was not in use, and in order to equalise the temperature it was encased in fairly thick brickwork.

When the catalyst in the reactor became exhausted after about 1,000 hours of operation the whole vessel was disconnected and replaced by another containing fresh catalyst.

Sulphur reactor: The vessel in which the organic sulphur compounds were re-formed as sulphuretted hydrogen consisted of a 'churn' of approximately the same over-all dimensions as the methane reactor. It had no internal fittings apart from a grid to support the catalyst and suitable gas connections.

Various catalysts had been tried in this vessel, including one containing copper. It was now customary to use the exhausted and sulphided nickel catalyst from the methanisation stage heated to a temperature of 400-450°C.

Details of the efficiency of sulphur removal by this catalyst were not available.

Preparation of Catalyst. The catalyst containing 100 Ni + 15 MgO + 50 kieselguhr was prepared at Oberhausen-Holten as follows :-

Precipitation: The mixed nickel and magnesium nitrate solutions were precipitated at boiling temperature with a small excess of sodium carbonate solution, and the kieselguhr then added. After thorough mixing the whole was filtered and washed with water equivalent to 120 cc./gm. Ni.

Extrusion: The filter cake was extruded as rods 3 m.m. diameter by forcing it through a die by means of a gear pump. In the early stages there had been some lack of uniformity in the product because some separation of water occurred between the pump and the die, but this was overcome by putting an agitator at this point.

Drying: The drying of the rods was carried out on a gas heated belt which moved forward slowly and discharged the hardened rods from the far end.

Breaking: The dried rods were fed into a vertical cylindrical machine having an axial shaft on which turntables were

fixed. The rotation of the shaft caused the rods to be flung against the inner wall of the cylinder and so ensured that all fragile material was degraded and also produced a good yield of the required size of granule.

Reduction: The granules, graded 3-5 m.m., were reduced in batches in a vessel shaped like a large covered Buchner funnel. The reducing gas consisted of 3:1 hydrogen-nitrogen mixture (obtained from the adjacent ammonia plant) preheated to 300-350°C. At the end of the reduction process the catalyst was cooled in reducing gas to 100°C. and further cooled in carbon dioxide. Catalyst prepared in this way could be handled in air for a sufficiently long time to allow filling of a reaction vessel without deterioration of the catalyst.

Kieselguhr: This was obtained from the Vereinigte Deutsche Kieselguhrwerke, Hanover. It was 'burned' by the suppliers in the ordinary way to a temperature believed to be about 1000°C. The product, which was not acid washed, contained some sand and no soluble iron.

Operating Conditions.

Catalyst temperature: It was said that methanisation was carried out at a temperature of 160-180°C., and it was considered important that the temperature should not rise much higher than this if carbon deposition was to be avoided and water jacket temperatures kept within easily manageable limits.

It was recognised that during normal working the heat of reaction might take the catalyst temperature appreciably above that of the jacket. The activity of the catalyst at these low temperatures, however, appears to be confirmed because, it was stated, the plant could be reliably re-started after a shut-down when the catalyst was ^{definitely} at a temperature of 160-180°C. and the inlet gas was at a lower temperature.

It was stated that there was no appreciable loss of nickel from the catalyst under these conditions.

Space velocity: When the amount of carbon monoxide in the town's gas was less than 5 per cent. a single reactor, containing about 160 litres of catalyst space, was capable of methanising the whole 180 cu.m./hr. With higher proportions of carbon monoxide the gas throughput was maintained but two reactors were used in parallel.

Steaming: When the carbon monoxide content of the gas exceeded 10 per cent. steam was introduced into the sulphur reactor to oxidize some of the carbon monoxide to dioxide and to increase the hydrogen content.

A recommended amount of steam was that which would be required to saturate the gas at 30-40°C.

Thermal efficiency. The following data relates to the plant at Altenessen.

1. The gas used for heating the reactors etc. was 6.4 per cent of the total input.

maximum theoretical
2. The ~~thermal~~ value of the methanised gas was 94 per cent. of that of the gas processed, equivalent to 88 per cent. of the total gas used.

3. The actual thermal recoveries were 84 and 78.6 per cent. respectively.

Design of larger plant. Dr. Traenckner said that although Ruhrgas hoped to use the process for other purposes and on a larger scale they had no such schemes prepared.

Attention is however drawn to the fact that during an interview with Dr. Kurt Haver of the A.G. der Kohlenwerstoff Verbande, Buchum (referred to in the report on targets 30/7.06, 30/73 by H.H. Lowry, H.J. Rose and E.T. Wilkins) a drawing by Demag dated 8.12.42 was produced. A copy of this drawing is available in Bag 1481, K.W.V. Item 5. A.G.K.V. professed to know nothing about this drawing except that it concerned a Ruhrgas methanisation project.

The dimensions of the plant illustrated in this drawing are several times larger than those of the plants previously described. It is not yet known, however, whether this plant was an alternative design for a 180 c.m./hr. plant or whether it was intended for use with a larger gas throughput or with gas other than coal gas. In this connection it may be significant that whereas drawings of smaller plants were inscribed with the code-word "Promotor", the Demag drawing was inscribed "Permagas".

Further information. Dr. Martin offered all possible assistance. Dr. Roehlen, who had been largely responsible for developing the process, was not available and according to Dr. Martin the most knowledgeable person on the subject was Dr. Rohe, a lawyer who was in charge of an establishment at Reelkirchen, near Hanover, where all records were stored.

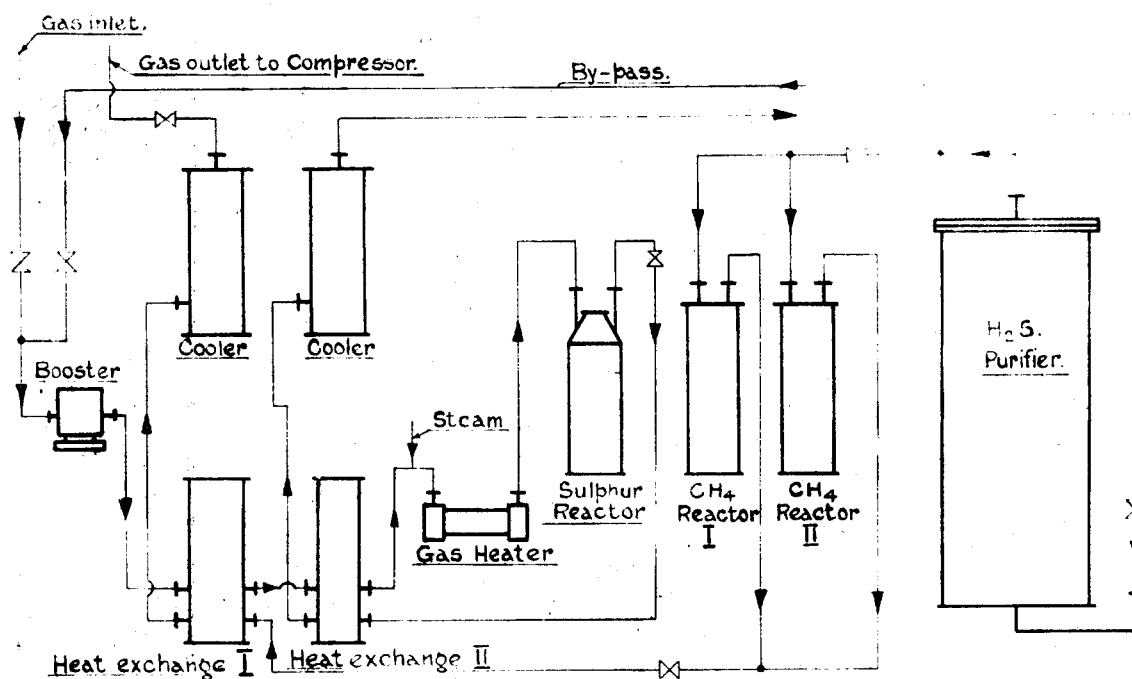


FIG. 1. METHANISATION OF TOWN'S GAS.
FLOW DIAGRAM OF RUHRGAS-RUHRCHEMIE PROCESS.

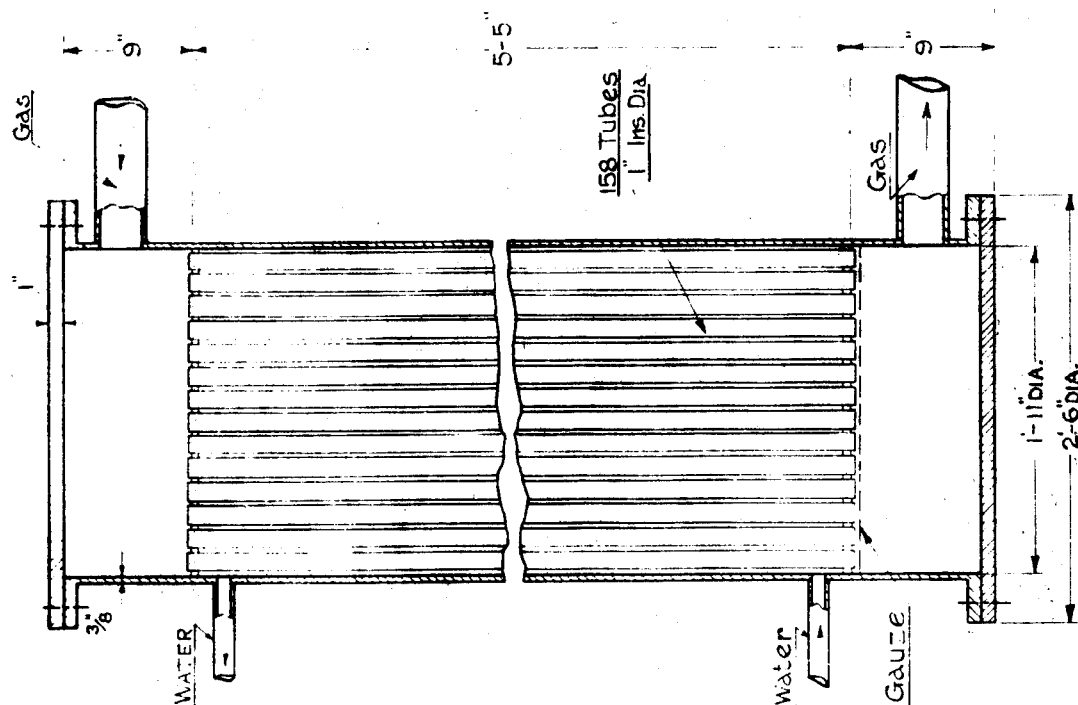


FIG. 2. METHANE REACTOR.
(Approx. to scale.)